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Gold(III) alkyne complexes: bonding and reaction pathways

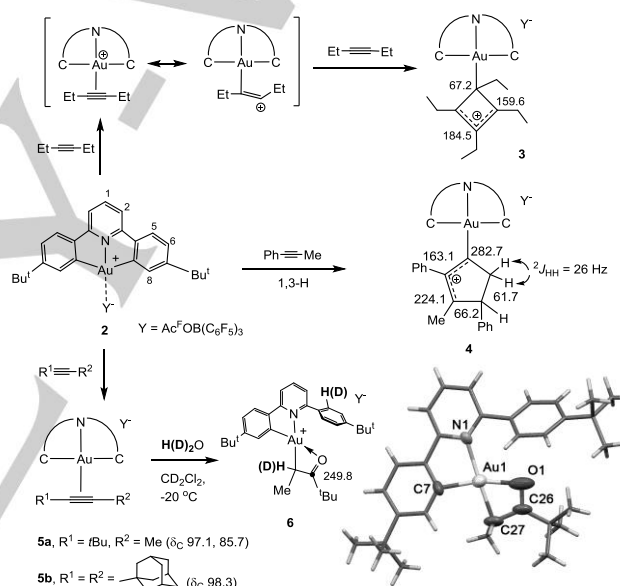
Luca Rocchigiani,^{*,[a]} Julio Fernandez-Cestau,^[a] Gabriele Agonigi,^[a] Isabelle Chambrier,^[a] Peter H. M. Budzelaar,^{*,[b]} and Manfred Bochmann^{*,[a]}

Abstract: The synthesis and characterization of hitherto hypothetical Au(III) π -alkyne complexes is reported. Bonding and stability depend strongly on the trans effect and steric factors. The bonding characteristics shed light on the reasons for the very different stabilities between the classical alkyne complexes of Pt(II) and their drastically more reactive Au(III) congeners. Lack of back-bonding facilitates alkyne slippage which is energetically less costly for gold than for platinum and explains the propensity of gold to facilitate C-C bond formation. Cycloaddition, followed by aryl migration and reductive deprotonation, are new reaction sequences in gold chemistry.

The reactions of gold complexes with alkynes form the basis of a multitude of organic catalytic transformation involving starting materials with C \equiv C triple bonds.^[1] Invariably these reactions are initiated by coordination of the alkyne to the metal, which induces polarization and susceptibility towards nucleophilic attack. Remarkably, unlike alkyne adducts of gold(I), which have been known since the 1970s,^[2-4] alkyne π -complexes of gold(III) have remained unknown.^[4] This is in sharp contrast to alkyne compounds of isoelectronic platinum(II), which were first reported over 50 years ago and provide textbook examples of the Dewar-Chatt-Duncanson π -bonding model.^[5-6] Elucidating the reaction chemistry of gold(III) has provided major challenges and has highlighted that drawing mechanistic analogies between gold(III) with the chemistry of isoelectronic Pd and Pt systems is often not valid.^[7-9] We show here that the hitherto elusive Au(III) alkyne complexes can in fact readily be generated and have Au-alkyne bond energies comparable to those of platinum, but are drastically more reactive. The results have enabled the first experiment-based comparison of alkyne bonding in Au(III) and Pt(II) systems and shed light on their reactivity differences, which helps explain the superior performance of gold in alkyne catalysis.

The reaction of (C^NC)AuOAc^F (OAc^F = trifluoroacetate) **1**-OAc^F with B(C₆F₅)₃ in dry dichloromethane generates the ion pair [(C^NC)Au...Y] [Y = Ac^FOB(C₆F₅)₃] **2** (Scheme 1). Internal alkynes were added to these solutions at -78 °C and the mixture was monitored by ¹H NMR spectroscopy at -20 °C. The outcome of the reactions proved to be dramatically affected by nature of the substituents at the triple bond (Scheme 1). With

sterically less hindered alkynes [2+2] cyclodimerization occurs. In the case of 3-hexyne this leads to the gold-bound cyclobutenyl cation **3**, whose structure and intermolecular contacts were elucidated by 2D NMR methods (see Supporting Information). By contrast, the interaction of 1-phenyl-1-propyne with **2** leads to a complex NMR spectrum consistent with the formation of the cyclopentenyl complex **4**, apparently produced by a combination of cyclodimerization and 1,3-H shifts.^[10,11] The observed ¹³C NMR data are in excellent agreement with the calculated NMR chemical shifts for complexes **3** and **4** (see Supporting Information). These cyclizations are an expression of the vinyl cation character of Au(III) alkynes and reflect the tendency for C-C bond formation that typifies gold catalyzed alkyne reactions.



Scheme 1. Formation and reactivity of Au(III) alkyne complexes, including ¹³C NMR chemical shifts of the product complexes (CD₂Cl₂, -20 °C). The structure of **2** indicates the numbering system used for NMR assignments. Crystal structure of **6**[SbF₆]·CH₂Cl₂, selected bond distances [Å] and angles [°]: N1-Au 2.13(1), C7-Au 2.06(2), Au-O1 2.09(2), Au-C27 2.07(2), O1-C26 1.23(2), N1-Au-C7 81.8(7), C7-Au-C27 100.6(9), C7-Au-O1 166.7(7), N1-Au-C27 174.9(8), C27-Au-O1 66.2(8), O1-Au-N1 111.2(6), O1-C26-C27 110(2). The angle through best planes of pyridine and the C₆H₄tBu ring is 46°.

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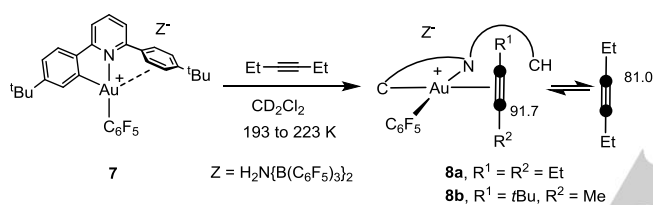
Supporting information for this article is given via a link at the end of the document. CCDC 1559726 (**6**) and 1569528 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cycloaddition is suppressed by steric hindrance. For example, mixing **2** with ca. 2.5 molar equiv of ^tBuC \equiv CMe or AdC \equiv CAd showed that only 1 equiv of alkyne reacted to give the π -complexes **5a** and **5b**, respectively, without cyclodimerization.^[11,12] Complexation was confirmed by the ¹³C NMR and the selective dipolar interactions of the Me and ^tBu substituents with the pincer ligand in the ¹H NOESY NMR spectrum. Alkyne coordination induces only modest ¹³C NMR shifts: **5a**: C(Me) δ_C = 85.7 ($\Delta\delta_C$ = 11.9 ppm); C(^tBu) δ_C = 97.1 ($\Delta\delta_C$ = 9.4); **5b**: δ_C = 98.3 ($\Delta\delta_C$ = 10.6), very similar to the values observed for [(R₃P)Au(alkyne)]BF₄.^[13] Solutions of **5a** show no exchange between free and coordinated alkyne and are stable for hours at -30 °C but decompose at 25 °C within minutes. By contrast,

the even more bulky bis(1-adamantyl)acetylene complex **5b** is stable for days in solution at room temperature and can be isolated as a yellow microcrystalline solid.^[11]

Gold(III) is well known for its ability to catalyze alkyne hydration.^[2a] This process is modelled by **5**, which reacts with water at -20 °C to give the ketonyl complex **6**. Evidently the proton released after the nucleophilic attack of H₂O at the alkyne cleaves the pincer. The same complex was obtained directly from **1-Cl**, AgSbF₆, ^tBuC≡CMe and H₂O (D₂O), in >90% yield. The structure was confirmed by X-ray diffraction (Scheme 1).

A second type of alkyne complexes could be generated after Au-C bond cleavage of **1-C₆F₅** with [H(OEt)₂][H₂N(B(C₆F₅)₃)₂] in C₆D₅Cl, followed by removal of associated Et₂O.^[14] Ether-free **7** reacts with 3-hexyne at -78 °C in CD₂Cl₂ to generate **8a** (Scheme 2). Alkyne coordination was indicated by a significant shift in the ligand signals. In this type of compounds the π-ligand is *trans* to an anionic C-atom, which, unlike the pyridine donors in **3** - **5**, exerts a strong *trans* influence, resulting in substantial weakening of the Au-alkyne bond.



Scheme 2. Generation of C^N chelated alkyne complexes.

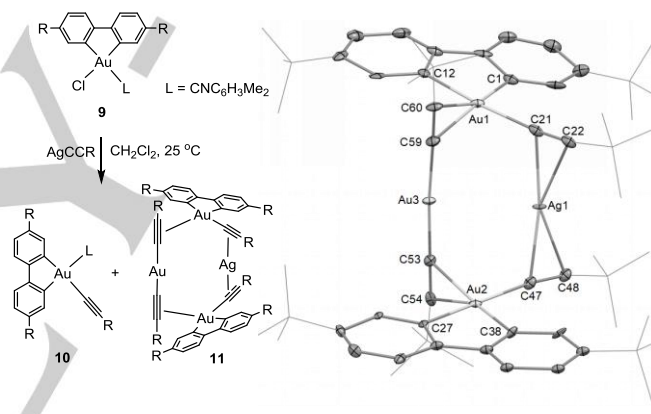
At -50 °C, 3-hexyne coordination to **8a** is strong enough to allow separate observation of the ethyl signals of bound and free alkyne. The ¹³C NMR signal of the coordinated triple bond was located at δ_C = 91.7 (Δδ_C = 10.7 ppm). ¹H NOESY NMR experiments revealed the presence of chemical exchange, indicating that the complex is still fluxional at -50 °C. Raising the temperature broadens the resonances, and coalescence between free and bound 3-hexyne occurs at about -30 °C. The simulation of the VT ¹H NMR spectra of **8a** allowed the activation parameters of alkyne exchange to be estimated, ΔH[‡] = 19.9 kcal/mol and a positive ΔS[‡] = 34 cal mol⁻¹ K⁻¹, suggesting that the exchange has a dissociative character. For the ^tBuC≡CMe complex **8b**, well-resolved spectra were obtained at -60 °C, allowing complete NMR characterization and a direct comparison with complex **5**, where the alkyne is *trans* to a pyridine donor. The alkyne ¹³C signals of **8b** are very similar to those of **5**; there is no detectable *trans* influence on the ¹³C NMR chemical shifts.

While these alkyne complexes have so far resisted all attempts at crystallization, structural confirmation of alkyne bonding was unexpectedly obtained from the reaction of **9**^[15] with AgC≡C^tBu, which gives two thermally stable crystalline products, **10** and **11**. The latter, a product of partial reduction, contains a π-bonded Au(C≡C^tBu)₂ anion which, probably due to packing effects, displays two types of Au(III)-alkynyl interactions: one symmetrical Au(III)-alkynyl bond with an elongated C≡C distance of 1.23(3) Å, and an asymmetric alkynyl bridge with two

very different Au^{III}-C distances (2.29(2) and 2.52(2) Å) and which lacks the C≡C bond elongation (Scheme 3).

The bonding of alkynes to Au(III) was explored by Density Functional Theory (DFT) calculations (Gaussian 09, TPSSH/cc-pVTZ// B3LYP/SVP), and compared to bonding in structurally related Pt(II) fragments.^[16] Surprisingly, the dissociation energies of Au(III) and Pt(II) with pyridine ligands in *trans* position were remarkably similar, suggesting that the observed differences in reactivity are not due to thermodynamic effects. Alkyne bonding to [(C^N-CH)Au(C₆F₅)]⁺ was weaker by 30-40 kcal/mol compared to [(C^N^C)Au]⁺, for both electronic and steric reasons: the empty coordination site in [(C^N-CH)Au(C₆F₅)]⁺ is *trans* to a strong Au-C bond, and it is shielded by the dangling aryl arm. General bonding trends are very similar between the two types of complexes, with the more π-donating alkynes binding most strongly.

The Au(III)-C(alkyne) bond distances calculated for the model [(C^N^C)Au(2-butyne)]⁺ correspond remarkably closely to those found for the π-bonded alkynyl ligand in **11** (Figure 1)



Scheme 3. Formation of the p-bonded Au(III) alkynyl complex **11**. Hydrogen bonds are omitted for clarity; ellipsoids are drawn at 50%. Selected bond distances [Å] and angles [°]: Au1-C59 2.33(2), Au1-C60 2.40(2), Au1-C21 1.98(3), Au2-C53 2.29(2), Au2-C54 2.52(2), Au2-C47 2.07(2), C53-C54 1.17(3), C59-C60 1.23(3); C53-Au3-C59 175.6(9), Au1-C60-C59 72(1), Au1-C59-C60 78(1), Au2-C53-C54 87(2), Au2-C54-C53 65(2).

Table 1. Calculated alkyne dissociation free energies from gold(III) and platinum(II) fragments (kcal/mol).^{[a][11]}

Ligand	[(C ^N ^C)Au] ⁺	[(C ^N ^N)Pt] ⁺	[(C ^N ^CH)Au(C ₆ F ₅)] ⁺
CO	46.5	55.7	8.5
HC≡CH	38.9	41.7	4.3
MeC≡CMe	48.7	47.6	12.3
EtC≡CEt	53.0	50.8	15.0
MeC≡C ^t Bu	53.1	51.0	13.4
MeC≡CPh	50.6	49.7	13.8

^[a] C^N^N = 2,2'-bipyridyl-6-C₆H₄.

In order to assess the *trans*-influence on back-donation, charge decomposition analysis was carried out.^[17] Back-donation for all gold(III) compounds is very low and is further reduced by strong *trans* ligands; e.g. **5** shows a back-donation/donation (B/D) ratio of 0.43, which drops to B/D = 0.17

for **8a**, much less than in structurally analogous $[(C^{\wedge}N^{\wedge}N)Pt^{II}(3\text{-hexyne})]^+$ ($B/D = 0.77$). The stability of alkyne complexes depends almost entirely on π -donation from the triple bond. We ascribe the relative stability of **8** and the reduced tendency of this complex to undergo [2+2] cycloaddition to the steric shielding provided by the "Pacman"-type $C^{\wedge}N$ -aryl ligand structure, which provides a kinetically protected binding pocket and thus enables detection of these thermodynamically labile species.

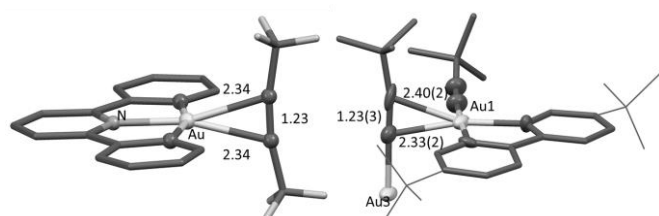


Figure 1. Comparison of Au-C and C-C distances of the calculated model $[(C^{\wedge}N^{\wedge}C)Au(2\text{-butyne})]^+$ (left) and the π -alkynyl fragment of the crystal structure of **11**.

The lability of Au(III) alkyne complexes and their high reactivity contrasts sharply with the thermal and chemical stability of their Pt(II) analogues. Surprisingly, the alkyne binding energies to Au(III) are comparable to or slightly higher than those to Pt(II): -50.3 kcal/mol for $[(C^{\wedge}N^{\wedge}C)Au(3\text{-hexyne})]^+$, versus -42.6 kcal/mol for $[(C^{\wedge}N^{\wedge}N)Pt(3\text{-hexyne})]^+$. However, the reduced back-bonding permits more facile alkyne slippage, with consequent accumulation of positive charge on the β -carbon atom and an increase in its susceptibility to nucleophilic attack.

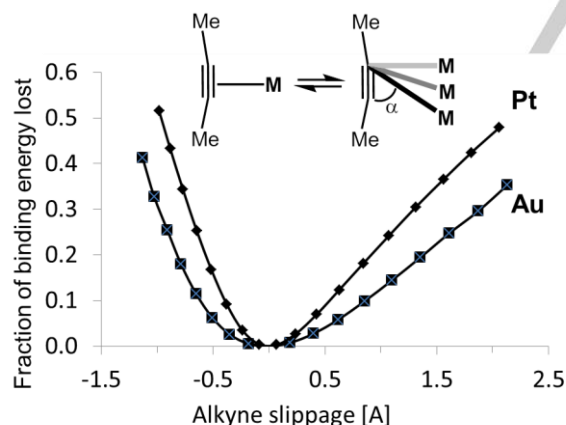


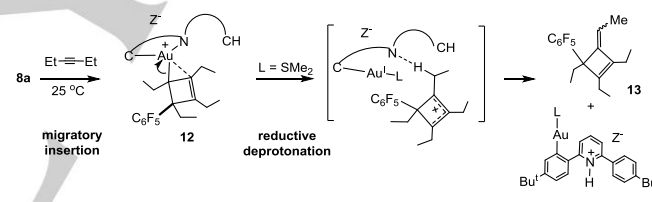
Figure 2. Fraction of binding energy lost vs 2-butyne slippage (Å) for $AuCl_3$ (■) and $PtCl_2(H_2O)$ (◆).

Alkyne slippage was probed using 2-butyne adducts of $AuCl_3$ and of $PtCl_2(H_2O)$ as models, by varying the angle α in the range $35^\circ - 120^\circ$ with steps of 5° , resulting in slippage values of ~ -1 to $+2$ Å (Figure 2).^[18] In the (non-slipped) π -complexes this angle is close to 75° and 73° for $Cl_3Au(butyne)$ and $trans\text{-}Cl_2(H_2O)Pt(butyne)$, respectively. Back-bonding can be expected to increase the barrier to geometric deformation, and indeed, at a slippage of $+1$ Å, the Au complex has lost only 13% of its acetylene binding energy, while the Pt complex has lost 23% (Figure 2). We believe this easier deformation of Au complexes

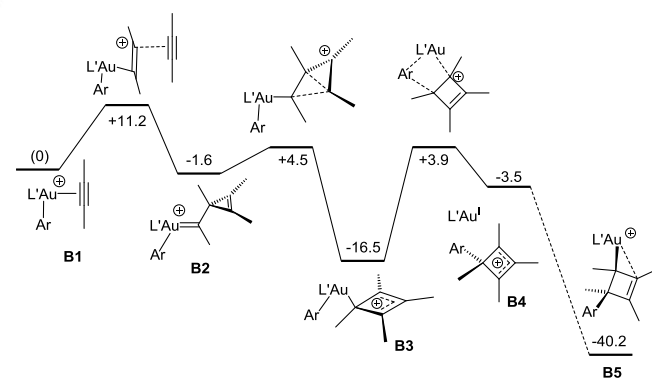
contributes significantly to the higher reactivity of gold(III) acetylene complexes.

Warming a mixture of **8a** and 3-hexyne to room temperature gives the thermally stable product **12** (Scheme 4). Its formation involves [2+2] cycloaddition, followed by C_6F_5 migration to the resulting cyclobutenyl cation. The C=C bond is significantly polarized due to a weak interaction with the gold centre ($\delta_C = 138.0$ and 185.1 ; cf. calculated values (Me model): $\delta_C = 131.4$ and 189.3). This reaction sequence – alkyne cycloaddition followed by migratory insertion into an Au-C(aryl) bond – is to the best of our knowledge unprecedented in gold chemistry.

Alkenes are typically released from metal alkyls by β -H elimination, as recently shown for gold(III) n -alkyls.^[8c] This process requires a vacant site in *cis* position and is suppressed by donor ligands. By contrast, alkene release from **12** is actually induced by donors (SMe_2 or $xylylNC$). Monitoring **12**/ SMe_2 mixtures at $-30^\circ C$, where the reaction is quite slow, showed no evidence for the formation of a transient Au(III)–H species,^[9b-d] nor was there evidence for a C(aryl)–H coupling product resulting from such an intermediate. On the other hand, a broad signal at $\delta_H = 13.4$ appeared, typical of a protonated pyridine. These findings suggest that **12** may follow an alternative path, *reductive deprotonation*, involving dissociation into a gold(I) aryl and a cyclobutenyl cation (Scheme 4), likely assisted by stabilizing SMe_2 coordination to Au(I), followed by deprotonation of the cyclobutenyl cation by pyridine to give **13** as an *E/Z* mixture.



Scheme 4. Reactivity of alkyne complexes: C-C coupling and alkene release.



Scheme 5. Free energy profile (298 K, chlorobenzene) for cyclodimerization and formation of **12**.

The free energy pathway for alkyne dimerization and cyclobutenyl-aryl coupling is shown in Scheme 5. Starting with the mono-alkyne π -complex **B1**, the Au atom moves to one of the two sp -C atoms, creating a gold-bound vinyl cation, which attacks a π -bond of a second alkyne. The resulting cyclopropenylmethylenecation **B2** is a shallow local minimum.

Opening of one of the two ring single bonds leads to the aured cyclobutenyl cation **B3**. The rate-limiting step is the initial alkyne-alkyne coupling. The transition state for coupling of the C_6F_5 and cyclobutenyl fragments (**B3** to **B4/B5**) looks somewhat like insertion of cyclobutadiene in the $Au-C_6F_5$ bond. The calculated barrier of ~ 20 kcal/mol indicates that this reaction should be rather slow at room temperature, as was indeed observed. The product **B4** formed immediately from the transition state resembles a combination of neutral (η^1-C^N-CH)Au(I) (with a long $Au\cdots N$ distance of 3.04 Å) and a cyclobutenyl cation, which would constitute an intramolecular redox reaction. This pair of species easily collapses to rather stable Au(III) cyclobutenyl complex **B5**. We suspect a direct route from **B3** to **B5** is avoided because that leads to an unfavourable isomer with the newly formed Au-C bond *trans* to that of the C^N-CH ligand. With additional stabilisation by SMe_2 , intermediate **B4** may also provide a pathway for the release of the organic product by reductive deprotonation (for the possibility of alkene release by β -H elimination see Supporting Information).

In conclusion, several distinct types of well-defined gold(III) alkyne complexes are now accessible and have been characterized by spectroscopic, structural and computational methods. Their synthesis has enabled an outline of their reaction pathways. Alkyne bonding is subject to a strong *trans* influence: ligands *trans* to pyridine-N are bound significantly more strongly than *trans* to an anionic C-donor. Although Au(III) and Pt(II) alkyne adducts show comparable binding energies, the much lower back-bonding in Au(III) complexes reduces the energy cost of alkyne slippage and facilitates $C\equiv C$ bond polarisation. This greatly enhances the susceptibility of gold-bound alkynes towards nucleophilic attack and C-C bond formation, in line with the behaviour of gold catalysts. Overall, gold(III) alkyne complexes display reaction pathways which are unprecedented in gold chemistry and illustrate the drastic reactivity differences between gold(III) compounds and their Pt(II) congeners.

Acknowledgements

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Keywords: Gold • alkyne • bonding • reaction mechanisms • density functional calculations

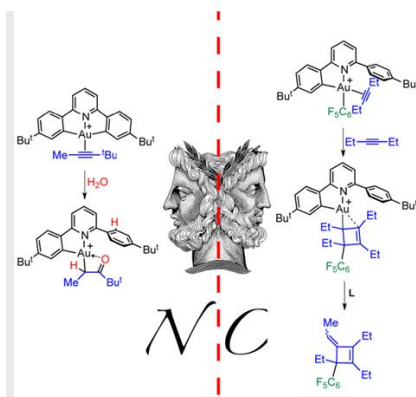
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The synthesis of hitherto hypothetical gold(III) π -alkyne complexes highlights the differences between classical platinum alkyne complexes and their drastically more reactive Au(III) congeners.



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Gold(III) alkyne complexes: bonding and reaction pathways

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